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**Request
for
Continued Examination (RCE)
Transmittal**

Address to:
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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Application Number	10/27,708
Filing Date	12/04/2003
First Named Inventor	Zhenan Bao
Art Unit	2814
Examiner Name	Douglas A. Wills
Attorney Docket Number	SAO 30

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1992, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

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 - a. Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.
 - i. Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
 - ii. Other _____
 - b. Enclosed
 - i. Amendment/Reply
 - ii. Affidavit(s)/Declaration(s)
 - iii. Information Disclosure Statement (IDS)
 - iv. Other _____
2. Miscellaneous
 - a. Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of _____ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(e) required)
 - i. Other _____
3. Fees
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 - ii. Extension of time fee (37 CFR 1.135 and 1.17)
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SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

Signature	Ronald J. Carter	Date	06/27/05
Name (Print/Type)	Ronald J. Carter	Registration No.	47,500

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Signature	Marty Bello	Date	06/29/2005
Name (Print/Type)	Marty Bello	Registration No.	

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PAGE 313 * RCVD AT 7/13/2005 10:38:52 AM (Eastern Daylight Time) * SVR:USPTO-EFXP-176 * DMS:2733308 * CSD:9724808865 * DURATION (min:sec):05:30

22/2005 LWISE1 00000001 082395 10727709

FC:1801 790.00 DR

Adjustment Date: 09/29/2005 SDIRETA1
07/22/2005 LWISE1 00000001 082395 10727709
01 FC:1801 790.00 CR

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ATTORNEY DOCKET NO.: BAO, BY

NO. 1639 P. 2
PATENT

PATENT AND TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Zhenan Bao, et al. 2005 AUG - 3 PM 3:15
RECEIVED
Serial No.: 10/727,709 US PATENT & TRADEMARK OFFICE CENTER
Filed: December 4, 2003 OFFICE AUG 03 2005
Title: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS
FORMED OF DENSIFIED LAYERS
Group Art Unit: 2814
Examiner: Waisong Louie

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Marty Bell
Printed or typed name of person signing the certificate
8-3-05 *Marty Bell*
Date of Mailing Signature of person mailing

Sir:

REQUEST FOR REFUND

On June 30, 2005 we filed an RCE and Foreign Search Information Disclosure Statement via facsimile to the USPTO in connection with the above-referenced case (see Attachment A). As you can see, on our Deposit Account Statement of July 2005 (see Attachment B), we were charged twice for the RCE fee: once on July 12, 2005 and the second time on July 22, 2005. We therefore request that the refund of the second RCE fee of \$790.00 which was withdrawn from the deposit account be refunded to our deposit account 082395.

Respectfully submitted,

HITT GAINES, P.C.

Ron Corbett
Ronald J. Corbett
Reg. No. 47,500

Date: August 3, 2005

Hitt Gaines, P.C.
P.O. Box 832570
Richardson, Texas 75083-2570
(972) 480-8800

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NO. 1639 P. 3

P. 1

* * * COMMUNICATION RESULT REPORT (JUN. 30. 2005 9:06AM) * * *

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FACSIMILE TRANSMISSION

TO: USPTO
Examiner Douglas A. Wille; Art Unit 2814
FAX NO. (571) 273-1721 (direct fax number for Examiner Wille)
FROM: Ronald J. Corbett
RE: Serial No.: 10/727,709
Attorney Docket No.: BAO 39
LUCT-125888
DATE: June 30, 2005
PAGES: 13 (including cover page)

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Thank you!

Marty Balko
(assistant to Ron Corbett)

Mailing Address: P.O. Box 232570, Richardson, Texas 75083-2570
Street Address: Palisades Central II, 2435 North Central Expressway, Suite 1300, Richardson, Texas 75080-2753 U.S.A.
Tel: (972) 480-8800 Fax: (972) 480-8845 fax@hittgaines.com

Attachment A

PAGE 3/17 * RCVD AT 8/3/2005 6:57:00 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-6/25 * DNIS:2738300 * CSID:9724808865 * DURATION (mm:ss):05:42

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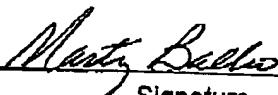
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Date

- Request for Continued Examination (RCE) Transmittal (pp 1);
- Foreign Search IDS (pp 2) with cited reference; and
- IDS by Applicant (pp 2).



Signature

Marty Balko

Typed or printed name of person signing Certificate

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**Request
for
Continued Examination (RCE)
Transmittal**Address to:
Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Application Number	10/727,709
Filing Date	12/04/2003
First Named Inventor	Zhenan Bao
Art Unit	2814
Examiner Name	Douglas A. Wille
Attorney Docket Number	BAO 39

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

1. **Submission required under 37 CFR 1.114** Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

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i. Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

ii. Other _____

b. Enclosed

i. Amendment/Reply

ii. Affidavit(s)/Declaration(s)

iii. Information Disclosure Statement (IDS)

iv. Other _____

2. **Miscellaneous**

a. Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of _____ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(l) required)

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3. **Fees**

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

a. The Director is hereby authorized to charge the following fees, any underpayment of fees, or credit any overpayments, to Deposit Account No. 08-2395. I have enclosed a duplicate copy of this sheet.

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SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED			
Signature	<i>Ronald J. Corbett</i>	Date	6/29/05 06/30/2005
Name (Print/Type)	Ronald J. Corbett	Registration No.	47,500

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Signature	<i>Marty Balko</i>	Date	06/30/2005
Name (Print/Type)	Marty Balko	Registration No.	

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DOCKET NO. BAO-39

AUG 03 2005 PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Zhenan Bao

Serial No.: 10/727,709

Filed: December 4, 2003

For: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS
FORMED OF DENSIFIED LAYERS

Group No.: 2811

Examiner: Douglas A. Wille

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

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Marty Bao
Printed or typed name of person signing the certificate
6-30-05 *Marty Bao*
Date of Mailing Signature of person mailing

Sir:

FOREIGN SEARCH INFORMATION DISCLOSURE STATEMENT

In accordance with 37 C.F.R. §1.56 and the provisions of 37 C.F.R. §§1.97 and 1.98 and §609 of the Manual of Patent Examining Procedure, Applicant hereby makes a disclosure of the patents, publications and other information listed below and on the accompanying form IDS by Applicant, which may be potentially material to the patentability of the invention disclosed in the above-referenced application. Pursuant to § 1.97(e) the Applicant hereby states that each item of information contained in the information disclosure statement was cited in a communication from a

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NO. 1639 P. 7

foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement.

U.S. Patent No.

5,546,889

Inventor

Wakita, et al.

Date

August 20, 1996

Other References:

YU-TAITAO, et al. "Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold", Langmuir, Volume 13, No. 15 (1997), pages 4018-4023.

As attorney for the Applicant, I am signing below on the basis of the information supplied by an individual designated in § 1.56(c).

The Commissioner is hereby authorized to charge any fees or credit any overpayments to Deposit Account No. 08-2395.

Respectfully submitted,

HITT GAINES, P.C.



Ronald J. Corbett
Registration No. 47,500

Date: June 30, 2005

Hitt Gaines, P.C.
P.O. Box 832570
Richardson, Texas 75083-2570
(972) 480-8800

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Sheet 1 of 2

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT <i>(Use as many sheets as necessary)</i>		Application Number	10/727,709
		Filing Date	December 4, 2003
		First Named Inventor	Zhenan Bao
		Art Unit	2811
		Examiner Name	Douglas A. Wille
		Attorney Docket Number	BAO -39
Sheet	1	of	2

Examiner Signature		Date Considered
Examiner's Signature		Date Considered

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Complete if Known

Complete if Known	
Application Number	10/727,709
Filing Date	December 4, 2003
First Named Inventor	Zhenan Bao
Art Unit	N/A
Examiner Name	Douglas A. Wille
Attorney Docket Number	BAO -39

NON-PATENT LITERATURE DOCUMENTS

Examiner Signature		Date Considered	
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Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold

Yu-Tai Tao,* Chien-Ching Wu, Ji-Yang Eu, and Wen-Ling Lin

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

Kwang-Chen Wu and Chun-hsien Chen†

Department of Chemistry, National Sun Yat-Sen University,
Kaohsiung, Taiwan 80424, Republic of China

Received January 31, 1997. In Final Form May 12, 1997

The structure of self-assembled monolayers of thiophenol (I), benzyl mercaptan (II), biphenylthiol (III), and 4-biphenylmethanethiol (IV) on the surface of Au(111) are compared using cyclic voltammetry, reflection absorption infrared spectroscopy, scanning tunneling microscopy, ellipsometry and contact angle measurement. The results suggest that benzyl mercaptan and 4-biphenylmethanethiol form closely packed and ordered monolayer, irrespective of the length of a *p*-alkoxy substituent. For thiophenol and biphenylthiol, a film of lower surface coverage was formed. A long *p*-alkoxy chain (*n*-C₁₂H₂₅O) increases the intermolecular interaction and leads to a closer packing within the monolayer film. The difference is attributed to the interplay between intramolecular interaction and the bond angle preference at the triolate head group.

Introduction

The self-assembling of organothiol on gold to form a monolayer has attracted much attention lately both from the fundamental point of view and from their application prospects.¹ In most applications, structural order and integrity of the film are of major concern. A simple alkaniethiol monolayer is one of the most thoroughly studied self-assembled monolayers (SAM) systems. Detailed structural information regarding the packing, orientation, as well as conformation of the molecular chains have been accumulated by various analytical techniques.²⁻⁶ The aromatic-containing monolayer is of importance because many optoelectronic applications involve an aromatic chromophore as the functioning unit. Many studies of aromatic-containing monolayers on gold have been reported, with the aromatic moiety as the only major component or as a part of a chain or in the presence of other functional groups.⁷⁻²⁷ It has been shown that such molecules anchor on gold substrates predominantly

through the sulfur atom instead of the aromatic ring.¹³ Nevertheless, a variety of structural details are proposed. It is noted that for the simplest member of the arylthiol, thiophenol, the detailed structure has not been unambiguously determined. On the basis of several methods, Sabatani *et al.*¹² concluded that thiophenol forms poorly defined microlayers. Well-ordered lattice structure was not found by high-impedance scanning tunneling microscopy (STM) for thiophenol monolayer either.¹³ With an increase of the number of aromatic moieties, the monolayers become either more densely packed or well ordered,^{14,15,16} presumably a result of stronger adsorbate-adsorbate interactions. The effect of a pending alkyl chain on the packing is not well understood.^{14,15}

In this paper we wish to report our further structural studies for monolayers formed by a series of aromatic-derivatized thiols, namely, I-IV (Chart 1), on gold in order

⁸ Abstract published in *Advance ACS Abstracts*, June 13, 1997.
(1) For a general review, see: (a) Ulman, A. *An Introduction to Ultrathin Organic Films*; Boston, MA, 1993. (b) Ulman, A. *Chem. Rev.* 1998, 98, 1533-1542.
(2) Parker, M. D.; Bright, T. B.; Alford, D. L.; Chidley, C. E. D. *J. Am. Chem. Soc.* 1927, 49, 3559-3568.
(3) Finkbein, W. D.; Arment, E.; Lynch, M.; Furtach, T. *Langmuir* 1987, 3, 408-418.
(4) Nuzzo, R. G.; Reggiani, B. R.; Dubois, L. K. *J. Am. Chem. Soc.* 1987, 109, 743-740.
(5) Nuzzo, R. G.; Trupke, L. S.; Tao, Y. T.; Eyll, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 521-535.
(6) Lubstein, P.; Whitesides, G. M.; Finkbein, A. N.; Tao, Y. T.; Alford, D. L.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1991, 113, 7152-7157.
(7) Walczak, M. M.; Chung, C.; Stole, S. M.; Wadri, C. A.; Parker, M. D. *J. Am. Chem. Soc.* 1991, 113, 2370-2378.
(8) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* 1991, 113, 5623-5637 and 5684-5693.
(9) (a) Strong, L.; Whitesides, G. M. *Langmuir* 1983, 4, 546-559. (b) Dubois, L. H.; Zeng, B. R.; Nuzzo, R. G. *J. Chem. Phys.* 1985, 82, 678-682. (c) Parker, P.; Elyashiv, P.; Li, J.; Camilliani, N. H.; Bartsch, S.; Sankar, G.; Ramamurthy, T. A.; Lynch, K. S. *Langmuir* 1991, 7, 2013-2018. (d) Somerton, M. G.; Parker, P. A.; Gardner, C. H. *Langmuir* 1991, 7, 497-436. (e) Chidley, C. E. D.; Liu, G.; Rovnaya, P.; Scobie, G. *J. Chem. Phys.* 1988, 81, 4421-4425.
(10) Wiggins, C. A.; Alves, C. A.; Parker, M. D. *J. Am. Chem. Soc.* 1981, 103, 2806-2810.
(11) Alford, D. L.; Smith, E. L.; Parker, M. D. *J. Am. Chem. Soc.* 1982, 104, 1222-1227.

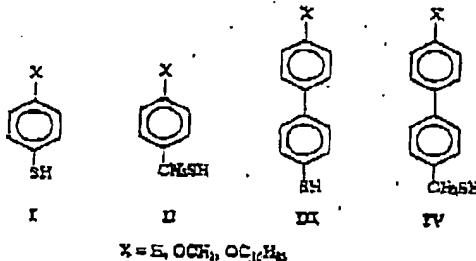
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Structure Evolution of Thiol Monolayers

Chart 1



to delineate factors that determine the structural order. Here the adsorbate-adsorbate interaction is manipulated in two ways. First, along the line of aforementioned packing promoted by intermolecular attractions, we systematically examine monolayer structures as a function of the number of rings involved and the length of the alkyl chain connected to thiolating. Second, we perturb the steric conformation of head groups by inserting one methylene unit in between the aryl and the mercapto group (i.e., compounds II and IV). The results show, for the first time, that the insertion of the methylene unit can turn ill-defined thiophenoxy monolayers into well-ordered SAMs of benzyl thioacetates. In addition, depending on the length of a para-substituted alkoxy group, various structural order and packing density were obtained for thiophenoxy. A simulation model derived by Sellars et al.¹⁰ is adopted to elucidate the discrepancy arising from the insertion of the methylene unit. The different behavior is attributed to a counterbalance of intermolecular interaction and bond angle preference at the sulfur atom (sp^3 versus sp^2).

Experimental Section

Materials. Thiophenoxy, mercapto, and benzyl mercapto were obtained from Aldrich and used directly. 4-Methoxybenzyl bromide, 4-biphenylmethanethiol, (4,4'-methoxybiphenyl)methanethiol and 4,4'-(hexaethoxy)biphenylmethanethiol were prepared by thionucleophilic substitution of corresponding benzyl bromide followed by hydrolysis.²⁰ The 4-biphenylthiol and 4,4'-ethoxybiphenylthiol were synthesized from corresponding aryl bromide by metal-halogen exchange followed by sulfur quench. 4,4'-(Hexaethoxy)biphenylthiol was prepared by sodium ethanolate substitution of the corresponding bromide followed by selective dealkylation of the resulting thioether.²¹

Substrate Preparation. The gold substrates were prepared by vapor deposition of about 200 nm of gold (99.99% purity) onto freshly cleaved 1-in. mica sheets at a rate of 1 nm/s under a pressure of 9×10^{-6} Torr using an Ulvac 270-pumped evaporator. The vacuum chamber was back-filled with high-purity nitrogen after 45 min after deposition. The gold substrates were transferred to a furnace and annealed at 300 °C for 4 h. The roughness factor for substrates prepared under these condition was estimated to be 1.2.²² The gold substrates were cleaned in a UV ozone cleaner for 1 h and washed with ethanol right before these substrates were immersed in thiol solution. For IR measurement, 2-in. silicon wafers were used as the substrate in gold deposition. An adhesion layer of chromium (5–10 nm) was deposited before gold evaporation.

Monolayer Preparation. Thioles with one phenyl ring are dissolved in ethanol in a concentration of 1 mM. Compounds

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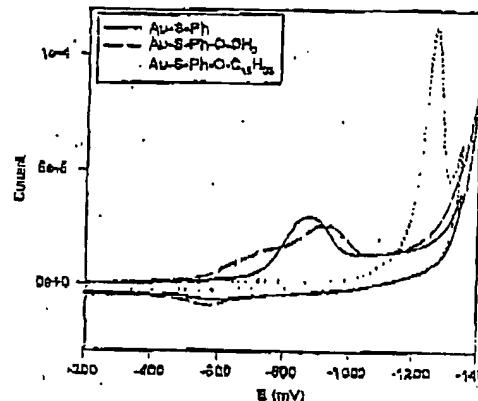


Figure 1. Cyclic voltammery curves for $\text{Au-S-C}_2\text{H}_5$, $\text{Au-S-C}_2\text{H}_5-\text{O-CH}_3$, and $\text{Au-S-C}_2\text{H}_5-\text{O-C}_6\text{H}_4\text{-CH}_3$ monolayers.

containing two aromatic rings are less soluble and were first dissolved in a minimum amount of THF, and then ethanol was added to make up the final solution of 0.26 mM. Substrates were immersed in solution for at least 24 h. Samples were washed with THF and ethanol successively and dried with a flow of argon gas or spin-dried prior to use.

Electrochemical Measurement. A CV-27 potentiostat or a 100S electroanalytic system (Biosanalytical Systems, West Lafayette, IN) was used in cyclic voltammery measurements. A conventional Pt-r-electrode cell was used with the area of the working electrode defined by the opening in an inert elastomer O-ring (0.66 cm²). A Pt coil auxiliary electrode and an Ag/AgCl/5 M NaCl reference electrode were used; all voltages were recorded with respect to this reference electrode. The supporting electrolyte was 0.5 M KOH (99.99% purity) in distilled, deionized water. The solution was purged with argon for 10 min prior to the experiment. The applied potential was cycled between -0.2 and -1.35 V at a scan rate of 100 mV/s with an initial potential of -0.2 V.

STM Measurements. STM measurements were carried out with a NanoScope II (Digital Instruments, Santa Barbara, CA) using a commercial Pt/Ir tip or a tungsten tip which was electrochemically etched to 1 M KOH. The images were calibrated by $\text{Au}(111)$ or HOPG (highly oriented pyrolytic graphite) in air.

Details of infrared measurements, ellipsometry measurements, and contact angle measurement were described previously.¹⁰

Results

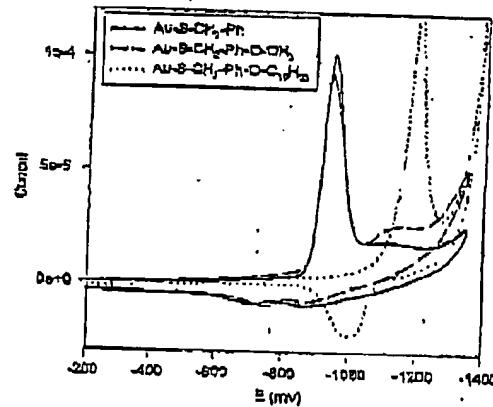
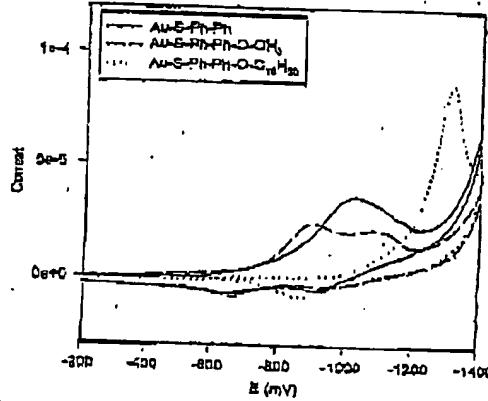
Electrochemical Measurement. The typical linear sweep voltammery curves for the four series of monolayers on Au are shown in Figures 1–4. A summary of the desorption peak potentials and calculated surface coverages is shown in Table 1. In general, the peak on the reductive scan represents the desorption of the monolayer from the gold electrode. The area under the peak relates the number of molecules that were reductively desorbed from the surface as thiolate assuming a one-electron reduction process²³ and is directly related to the surface coverage. The peak potential has been shown to depend on the hydrocarbon chain length of the thiolate and such dependence is suggested to be related to the potential required to establish a potential gradient through the film that induces an ion flux sufficient to support the reduction process. It is noted that for the series II and IV, all the desorption peaks are rather sharp and well defined, whether it is unsubstituted or substituted with alkoxy group of different length. Moreover, the surface

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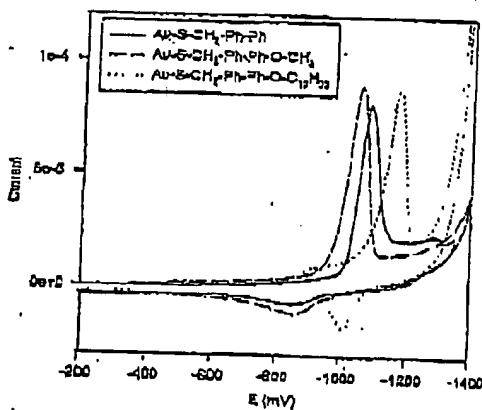
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Table 1. Packing Density ($\times 10^{-10}$ mol/cm 2) and the Desorption Potential (mV) in Parentheses of Aromatic-Derivatized Thiol on Evaporated Au Using Electrochemically Reductive Desorption Method

	I	II	III	IV
X = H	4.4 \pm 0.4 (-848)	8.1 \pm 0.3 (-921)	5.1 \pm 0.7 (-920)	8.0 \pm 0.3 (-1081)
X = OCH ₃	5.1 \pm 0.3 (-921)	8.1 \pm 0.3 (-920)	5.4 \pm 0.8 (-907)	8.0 \pm 0.1 (-1087)
X = OOC ₁₆ CH ₃	6.6 \pm 0.6 (-1215)	8.0 \pm 0.4 (-1162)	7.7 \pm 0.3 (-1305)	7.5 \pm 0.3 (-1167)

Figure 2. Cyclic voltammetry curves for Au-S-CH₃-C₆H₄ and Au-S-CH₃-C₆H₄-O-C₁₆H₃₃ monolayers.Figure 3. Cyclic voltammetry curves for Au-S-C₆H₄-C₆H₄ and Au-S-C₆H₄-C₆H₄-O-C₁₆H₃₃ monolayers.

coverages as calculated from the area under the peaks are similar irrespective of the substituent group on the aromatic ring. And the value is also close to that for the saturated n-hexadecanethiolate monolayer on gold, 7.8×10^{-10} mol/cm 2 , equivalent to $21.5 \text{ \AA}^2/\text{molecule}$. For n-hexadecanethiolate monolayer, an overlayer of $(\sqrt{3} \times \sqrt{3})R30^\circ$ was shown by various methods, and a packing density of 7.7×10^{-10} mol/cm 2 ($21.5 \text{ \AA}^2/\text{molecule}$) is expected for such an overlayer.²⁰ Thus compounds in these two series most likely occupy a similar lattice as that of n-hexadecanethiolate monolayer. The desorption potential shows a trend to become more negative with increasing substituent chain length in the same series. The trend is more significant for the monophenyl system

Figure 4. Cyclic voltammetry curves for Au-S-CH₃-C₆H₄-C₆H₄-O-CH₃ and Au-S-CH₃-C₆H₄-C₆H₄-O-C₁₆H₃₃ monolayers.

(~ 240 mV difference in going from unsubstituted or methoxy-substituted to hexadecyloxy-substituted) than the biphenyl system (~ 100 mV for the corresponding change). These are consistent with the increasing difficulty in the penetration of ions through the film during reduction.¹¹ The shorter (monophenyl) system is more sensitive to the addition of shielding layer than the longer (biphenyl) system. The desorption peak potential is also more negative for the biphenyl series than the monophenyl series, with the same substituent group. The trend again is more significant for short chain (or unsubstituted) derivatives than the long chain derivatives.

On the other hand, for series I and III, the desorption peak shapes for the unsubstituted and methoxy-substituted ones are rather broad and ill-defined. More than one peak was also observed. Only with the C₁₆-substituted ones, a sharper and well-defined curve was obtained. The packing density depends very much on the substituent group on the aromatic ring, ranging from 4.4×10^{-10} mol/cm 2 ($37.8 \text{ \AA}^2/\text{molecule}$) for biphenol to 8.6×10^{-10} mol/cm 2 ($25.2 \text{ \AA}^2/\text{molecule}$) for hexadecyloxy-substituted thiophenol. With the biphenyl system, the packing density increases from 5.1×10^{-10} mol/cm 2 ($32.6 \text{ \AA}^2/\text{molecule}$) for the unsubstituted one to 7.7×10^{-10} mol/cm 2 ($21.5 \text{ \AA}^2/\text{molecule}$) for the hexadecyloxy-substituted one. Thus for monolayers of series I and III with X = H, the coverages are only about 50% of that of a full ($\sqrt{3} \times \sqrt{3})R30^\circ$ monolayer, implying each molecule is occupying a larger average area than in the corresponding cases of II and IV. With increasing chain length of the substituent, the packing becomes denser. It is further noted that the desorption peak potentials do not differ by much between series I and III for the same substituent group, except for the long chain substituted one. This is in opposite trend as that observed for series II and IV, which could imply that the aromatic groups did not pack well in the adsorbed state to block the flux of ions during the reduction.

Infrared Reflection Absorption Spectra. Reflection-absorption IR spectra of monolayers of the four series

Structure Evolution of Thiol Monolayers

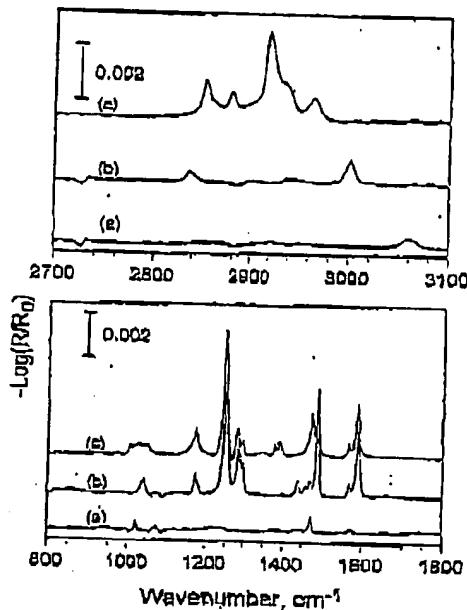


Figure 5. Infrared reflection absorption spectra for (a) $\text{Au-S-C}_6\text{H}_5$, (b) $\text{Au-S-C}_6\text{H}_4-\text{O-CH}_3$, and (c) $\text{Au-S-O-C}_6\text{H}_4-\text{O-C}_6\text{H}_5$ monolayers.

Table 2. Infrared Ring-Stretching Frequency of Aromatic-Derivatized Thiols on Evaporated Au and the Shift from Corresponding Value in KBr Sample, cm^{-1}

	I	II	III	IV
$\text{X} = \text{H}$	1472, -6	1494, 0	1475, -8	1488, 2
$\text{X} = \text{OCH}_3$	1488, -7	1518, 8	1479, -7	1601, 0
$\text{X} = \text{OC}_6\text{H}_5$	1488, -9	1514, 1	1475, 0	1501, 0

of compounds were taken. A representative series (for compound I) is shown in Figure 5. (The others are supplied as Supporting Information.) In general, the peak patterns in the C-H stretching region are very similar for the same substituent. Thus for C₆H₅ substituted case, the peak positions for methylene stretches (at 2915 and 2850 cm^{-1} respectively for II and shifted less than 2 cm^{-1} to higher end for the other three series) indicate close packing, if not a perfectly crystalline state of the chains. There are some variations in the relative intensities, which should be dependent on the exact chain tilt and twist. The methoxy-substituted ones all exhibit the same intensity for $\nu_{\text{as}}(\text{OCH}_3)$ at around 3002 cm^{-1} and $\nu_{\text{s}}(\text{OCH}_3)$ around 2880 cm^{-1} . The only major feature for the unsubstituted ones is a weak band around 8082 cm^{-1} , which is assigned as the aromatic C-H stretch. In the low-frequency region, of particular interest is the peak positions for the ring stretch mode occurring at around 1472–1518 cm^{-1} when compared to the KBr spectra of isotropic sample. The stretching frequency of the aromatic ring of monolayers I and III on Au shifted to lower values (by 6–9 wavenumbers) as compared to that in KBr spectra, except with $\text{X} = \text{C}_6\text{H}_5$ for III, whereas for monolayers of II and IV there is no change or a slightly positive shift in this ring-stretching frequency as compared to that in the KBr spectra (Table 2). The implication of these trends will be discussed later.¹¹

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Table 3. Ellipsometric Thicknesses of Aromatic-Derivatized Thiol Monolayers on Evaporated Au (Å)

	I	II	III	IV
$\text{X} = \text{H}$	1.3	2.4	9.6	10.5
$\text{X} = \text{OCH}_3$	1.8	5.2	10.4	13.0
$\text{X} = \text{OC}_6\text{H}_5$	22.3	25.2	30.6	33.3

Scanning Tunneling Microscopy Measurements. STM measurements show that the annealed bare gold substrates exhibit smooth plateaus with average size of ca. 50 nm in width. Images obtained on plateaus and terraces are composed of hexagonally close packed atoms with nearest-neighbor spacing of $2.9 \pm 0.3 \text{ \AA}$, indicative of $\text{Au}(111)$ orientation. All four series of thiols significantly affect the substrates, resulting in morphological features of pits and jagged step edges which are characteristic of ω -alkanethiol monolayers on gold.^{14,15} Because of the concerns of monolayer structures interfering with the STM tip due to the less conductive long alkyl chains, our report will concentrate on unsubstituted ones ($\text{X} = \text{H}$).

For monolayers of benzyl mercaptan (II), STM images always display a highly ordered hexagonal pattern. Figure 6a is a representative image obtained with 2 GΩ tunneling impedance (a bias voltage and tunneling current of 1.0 V and 0.5 nA, respectively). Under this condition, there is no indication of destructive imaging. Only one lattice structure is observed. The unit cell dimension is $4.9 \pm 0.1 \text{ \AA}$ and the angle between lattice vectors is $55 \pm 5^\circ$, consistent with a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure. The dark defect shown in the image also exhibits the same lattice parameters which can be seen clearly by adjusting the image contrast. For monolayers of 4-biphenylmethane-thiol (IV), the adlayer adopts preferentially a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure, although an unassigned local structure is also found.¹⁶ A typical image of the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure is presented in Figure 6b, which was obtained with 1 GΩ tunneling impedance. We notice that the imaging quality of series IV is, in general, not as decent as that of benzyl mercaptan (II). The origin of this difference is probably arising from the fact that the tunneling barrier of IV monolayers is an aryl ring thicker than those of II.

In contrast, for monolayers of series I and III with $\text{X} = \text{H}$ and OCH_3 , neither periodic pattern nor molecularly resolved images are observed, coherent with the finding of a previous STM study by Dhirani *et al.*¹⁶ In the case of (hexadecylxyl)phenylthiol (I with $\text{OC}_6\text{H}_5\text{H}_3$), we observed a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlayer in only a few occasions. The domain size is as small as ca. 4 nm. The film structure appears predominantly disordered.

Ellipsometric Thickness Measurement. The ellipsometric thicknesses of these monolayers are collected in Table 3. Qualitatively, the benzyl mercaptan derivatives (II and IV) are thicker, when compared with thiophenol analogues (I and III), presumably because of the additional CH_2 unit in the benzyl mercaptan system. The biphenyl systems (III and IV) are also thicker when

(a) Sander E. J.; Hirschbach, D. R. *J. Phys. Chem.* 1972, 76, 3277–3279.

(b) (a) Kim, Y.-T.; Bord, A. J. *Langmuir* 1992, 8, 1086–1107. (b) McElroy, R. J.; Dimmick, D. J.; Wilcock, R. J. *Langmuir* 1993, 9, 2773–2777. (c) Patten, C. E.; Trichin, M. J. *Langmuir* 1994, 10, 2559–2626. (d) Sander-Luetke, J. A. M.; Schonenberger, C.; Pethick, L. G. *J. Phys. Chem.* 1994, 98, 6826–6834.

(c) We have observed a local structure exhibiting step-and-modulation running across pits and line defects. The nearest-neighbor spacings along two primitive unit cell vectors are 4.0 ± 0.4 and $6.0 \pm 0.3 \text{ \AA}$ and the angle between the vectors is $88 \pm 7^\circ$. Although the pattern looks like a rectangle $\sqrt{3} \times \sqrt{3}$ structure, the area of the unit cell is too small to fit the high symmetry. At the present time, we are not able to assign a commensurate structure for this adlayer.

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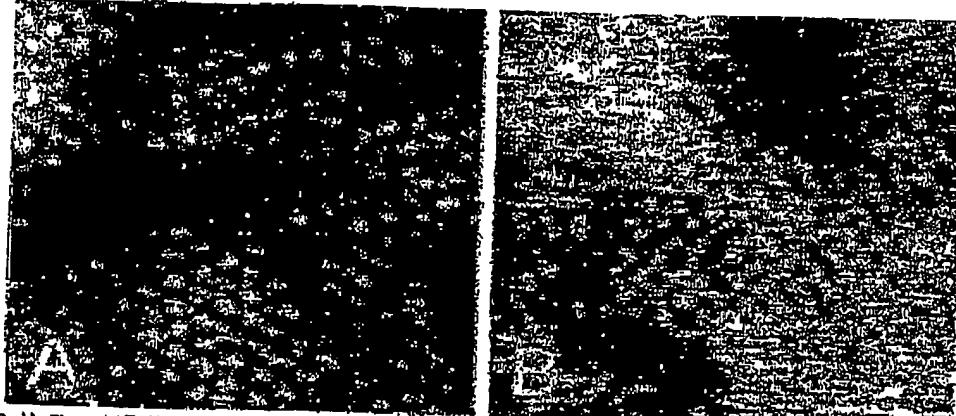


Figure 6. Unfiltered STM images of (a) $\text{Au-S-CH}_2\text{-C}_6\text{H}_5$ (image size $8 \times 8 \text{ nm}$, $i = 0.5 \text{ nA}$, $V_{\text{bias}} = 1.0 \text{ V}$, nearest-neighbor spacing $4.9 \pm 0.1 \text{ \AA}$) (b) $\text{Au-S-CH}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_5$; (image size $8 \times 8 \text{ nm}$, $i = 0.5 \text{ nA}$, $V_{\text{bias}} = 800 \text{ mV}$, nearest-neighbor spacing $4.9 \pm 0.3 \text{ \AA}$).

Table 4. Contact Angle (deg) of H_2O on the Aromatic-Derivatized Thiol Monolayers on Evaporated Au

	I	II	III	IV
$X = \text{H}$	70	63	80	89
$X = \text{OC}_2\text{H}_5$	88	84	50	66
$X = \text{OC}_6\text{H}_5$	109	112	112	111

compared with monophenyl analogues (I and II), as one would expect for the additional phenyl group in the biphenyl system. However, in an absolute sense, the observed thicknesses for the unsubstituted or short-chain substituted ones are thinner than the expected value from the dimension of the molecules involved. Furthermore, the difference between each series is more than that expected for the group involved (1.4 Å for a CH_2 group and 7 Å for a phenyl group). These may be due to the uncertainty associated with ellipsometry measurement (index of refraction, surface contamination on "bare" gold ..) as well as different packing density in each series, as evidenced by the electrochemical data. The ellipsometry data here can only serve as a qualitative support of the "monolayer" nature of the adsorbed film.

Contact Angle Measurements. Water contact angle values are reported in Table 4. It can be seen that the water contact angles on II and IV monolayers are higher than those on the analogues in I and III, but the difference decreases with increasing the length of X . While it can be argued that as the substituent chain length increases, the contact angle is less sensitive to the underlying substrate. It could also imply that the difference in the structure between I and II (or III and IV) diminishes as X increases in chain length.

Discussion

The data appear to fall into two categories. The first category includes benzyl mercaptans (II) and 4-phenylthiophenothiols (IV), both of which have a CH_2 unit between the thiol head group and the aromatic ring. They give well-defined cyclic voltammetry behavior in that the reductive wave is sharp and more uniform. The coverages correspond well to that of a close-packed n -alkanethiol monolayer. These adsorbates are expected to have a packing scheme similar to that of the n -alkanethiol, i.e., $(\sqrt{3} \times \sqrt{3})\text{RSO}^*$ overlayer, as also evidenced by STM

measurements. The second category includes thiophenols and biphenylthiols. In contrast with benzyl mercaptan, both thiophenol and *p*-methoxythiophenol gave a rather broad desorption peak and low surface coverage, which implies a rather ill-defined film structure and lower packing density. This is in agreement with STM observations and literature reports^{12,13} that thiophenol forms poor monolayers.²⁴

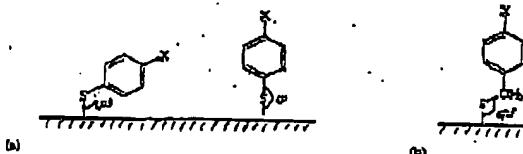
The discrepancy between these two categories shows the significance of the inserted methylene unit. For compounds containing the methylene unit, II and IV, the $(\sqrt{3} \times \sqrt{3})\text{RSO}^*$ lattice structure suggests the herringbone packing of phenyl or biphenyl moieties. Considering the dimension of the phenyl ring,²⁵ a herringbone packing will require the aromatic planes orienting nearly vertical to the gold surface.¹² This geometry was also suggested for adsorption of diphenyl disulfide on silver,²⁶ where the phenyl ring is "sticking up". For compounds without the methylene unit, I and III, the negative shifts in the IR frequency of the ring stretch mode region (from 1472 to 1515 cm^{-1}) are similar to that observed in the adsorption of diphenyl disulfide on silver,²⁶ where a "lying-flat" geometry was proposed based on Raman spectroscopy. This negative shift suggests that the long axis of the benzene ring (the one passing through X and S) for compounds I and III is inclined toward the gold surface. This tilt creates steric hindrance which would occupy a larger space and diminish intermolecular attractions between neighboring phenyl rings, and thus results in a poorly defined monolayer. Given the resemblance of these compounds, the methylene unit is an intriguing factor in orienting the phenyl ring vertical to the surface.

The critical role of the methylene unit can be illustrated by an S-Ar binding scheme modeled by the quantum calculations of Sellers et al.,²⁷ who proposed sp and sp^2 hybridization with surface-S-C bond angles of 180° and 104° , respectively. In the case of saturated n -alkanethiol on Au(111), the trend in the odd-even effect observed in

²⁴ It is noted that a different conclusion was obtained for biphenyl from electron transfer rate measurement.¹³ However, it is also noted in the same work that surface coverage measurements by ac impedance and gold oxide removal on a monolayer-covered surface indicates that biphenylthiol behaved more like thiophenol than thiophenol in the monolayer assembly.

²⁵ The van der Waals dimensions of a vertically oriented phenyl ring are 6.4 Å (width) \times 3.5 Å (thickness).

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(a) (b)
Figure 7. Possible orientation of monolayers of (a) thiophenol and (b) benzyl mercaptan derivatives on gold.

IR, δ , τ , ν which reflecting the orientation of the terminal methyl group, clearly implies a preference of sp^3 hybridization in the sulfur atom (or a $\text{Au}-\text{S}-\text{C}$ bond angle) and a trans zigzag extension of the alkyl chain. A linear $\text{Au}-\text{S}-\text{C}$ bond angle (or sp hybridization) has been invoked to rationalize a reversed trend in the odd-even effect observed on Ag .¹⁰ In the case of compounds I and III with $X = \text{H}$ and OCH_3 , the tilt orientation of phenyl ring implies that sp^3 hybridization is more favorable than sp hybridization (Figure 7a). For compounds II and IV, in order to adopt the close-packed ($\sqrt{3} \times \sqrt{3}$) R^2O structure, a bond angle of $\text{C}-\text{S}-\text{Au}$ is required. Consequently, sp^3 hybridization appears to be the favorable one for compounds II and IV as well (Figure 7b). In either category, the S atom adopts sp^3 hybridization when $X = \text{H}$ or OCH_3 . Therefore, the insertion of a methylene unit can relax the rigidity of the thiol head group and lead to a stronger intermolecular interaction.

For compounds I and III with a long chain substituent, such as a hexadecyl group, the electrochemical behavior is approaching that of the benzyl mercaptans. The same IR pattern in the CH stretching region also implies similar packing and orientation in the long alkyl chain portion. This would compel the long axis of the benzene ring to point nearly perpendicular to the surface. This is achieved by a greater surface-S-C bond angle or, equivalently, the adoption of sp hybridization at the sulfur atom, with energy compensated by a greater interchain interaction.

Langmuir, Vol. 13, No. 15, 1997, 4023

Conclusions

It is shown in this study that for phenyl-substituted thiols, the structure of a monolayer formed on gold is dependent on the location of the aromatic ring. With a methylene unit inserted between the phenyl ring and the thiol head group, a closely packed and ordered monolayer of ($\sqrt{3} \times \sqrt{3}$) R^2O structure can be formed. The substituent at the para-position increases the interchain interaction but does not grossly change grossly the packing density and/or arrangement. With a thiol group directly attached to the aromatic ring, the para-substitution affects the packing in the monolayer. In the absence of a substituent or in the presence of a short chain, a less densely packed monolayer with coverage as low as 80% of that of a fully packed monolayer can result. A longer chain introduces greater interchain interaction and results in a higher coverage. The difference between these two categories of thiols is suggested to be a balance of the interchain interaction and the binding geometry adopted at the thiolate head group. An sp^3 hybridization is suggested to be the favored state at the sulfur atom. This geometry allows the benzyl-type thiols to arrange the aromatic rings in a well-ordered packing but prohibits the thiophenol-type molecules to arrange their aromatic moiety. With a longer substituent at the para-position, greater packing interaction causes a change of bond angle (or a change of hybridization) to allow a tighter packing of the rings.

Acknowledgment Financial support from National Science Council, Republic of China, is gratefully acknowledged. C.H.C. gratefully acknowledges the Chemistry Department of National Sun Yat-sen University for a generous starting fund.

Supporting Information Available: Figures of infrared refraction absorbance spectra for II-IV monolayers (12 pages). Ordering information is given on any current masthead page.

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